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<p>(21) International Application Number: PCT/US96/20452</p> <p>(22) International Filing Date: 13 December 1996 (13.12.96)</p> <p>(30) Priority Data: 08/574,813 19 December 1995 (19.12.95) US</p> <p>(71) Applicant: MIDWEST RESEARCH INSTITUTE [US/US]; 425 Volker Boulevard, Kansas City, MO 64110 (US).</p> <p>(72) Inventor: PERN, Fu-Jann; 384 Flora Way, Golden, CO 80401 (US).</p> <p>(74) Agent: RICHARDSON, Ken; National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, CO 80401 (US).</p>		<p>(81) Designated States: AU, CN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).</p> <p>Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i></p>
<p>(54) Title: ENCAPSULATING MATERIAL FOR PHOTOVOLTAIC DEVICES</p> <p>(57) Abstract</p> <p>A substantially clear and substantially colorless encapsulating material for protectively encapsulating an operating photovoltaic device while substantially retaining light transmittal properties necessary for efficient device operation. The encapsulating material is substantially free of an ultraviolet light absorber component and comprises a polymer component and a curing agent component. Additional additives can include a primer component, an ultraviolet-light stabilizer component and an antioxidant component.</p>		

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Encapsulating Material for Photovoltaic Devices

5 The United States Government has rights in this invention under Contract No. DE AC36-83CH10093 between the United States Department of Energy and the National Renewable Energy Laboratory, a division of the Midwest Research Institute.

Technical Field

10 The present invention relates to an encapsulating material for protectively encapsulating an operating photovoltaic device and being substantially free of an ultraviolet-light absorber component.

Background Art

15 Because photovoltaic devices such as those incorporated in solar energy collectors are subjected to intense environmental impact including concentrated ultraviolet light exposure, yet must be able to efficiently receive sunlight with no or minimal blockage or dilution so that as much energy as possible can be extracted from this light source, it is important that adequate protective materials are available to
20 function as safeguards for photovoltaic devices without interfering with device operation. One such commonly-employed safeguard is an encapsulant material within which a photovoltaic device is housed. This material is formulated from ethylene vinyl acetate polymer, a curing agent component for the polymer, an ultraviolet light absorber component, an ultraviolet light stabilizer, and an antioxidant.

25 While the above-described prior-art polymer composition is widely employed, its longevity of utility with regard to clarity and clearness, two highly-important characteristics for adequate light transmission to the housed photovoltaic device, is severely limited. Specifically, it has been found that this material degrades relatively quickly to a yellow to dark brown color which, of course, interferes with full spectrum
30 solar admission to the encapsulated photovoltaic device. Since the encapsulated device as well as its polymer-composition encapsulant are usually sandwiched within cooperating structural-assembly pieces, changing the encapsulant is not practical. As a result, and after only a relatively short period of time, solar transmission to the

encapsulated photovoltaic device is permanently reduced and energy-collection efficiency drops dramatically.

In view of the above factors, it is apparent that a need is present for an encapsulating material having significant longevity. Accordingly, a primary object of the present invention is to provide an encapsulating material that maintains clear and colorless characteristics over a practical period of time.

Another object of the present invention is to provide an encapsulating material substantially free of any ultraviolet light absorber component, yet able to withstand normal ultraviolet light found in the solar spectrum without significant degradation.

These and other objects of the present invention will become apparent throughout the description thereof which now follows.

Disclosure of the Invention

The present invention is a substantially clear and substantially colorless encapsulating material for protectively encapsulating an operating photovoltaic device while substantially retaining light transmittal properties necessary for efficient device operation. The encapsulating material is substantially free of an ultraviolet light absorber component and comprises a polymer component and a curing agent component. Additional additives can include a primer component, an ultraviolet-light stabilizer component and an antioxidant component. As is apparent from a comparison of the prior art formulation recited above and the formulation of the present invention, the present material has no ultraviolet-light absorber material. Indeed, it has been discovered that such absorber material, always included in the prior-art compositions to convert ultraviolet light energy to heat energy, decomposes photochemically and contributes to or enhances browning of the encapsulating material to thereby significantly interfere with light transmittal through the encapsulating material. Non-inclusion of an ultraviolet absorber component in accord with the present invention results in the formulation of an encapsulating material whose clarity and color do not change substantially over a significant period of time, thereby significantly enhancing both the lifetime and the efficiency of a photovoltaic device as it operates to effectively capture solar energy.

Brief Description of the Drawings

Figure 1 is a graph comparing discoloration characteristics as measured by a yellowness index of four encapsulating-material formulations, each containing polymer, curing agent, ultraviolet-light stabilizer and antioxidant components, over a period of time expressed in hours; and

Figure 2 is a graph comparing discoloration characteristics of three encapsulating-material formulations, each containing polymer and curing agent only without additional additives, over a period of time expressed in hours.

Detailed Description of a Preferred Embodiment

The following examples describe the preparation of an encapsulating material for protectively encapsulating an operating photovoltaic device.

Example I

A stock solution of ethylene vinyl acetate is prepared by dissolving in an organic solvent such as cyclohexane, tetrahydrofuran, etc. a pre-weighed quantity of ethylene vinyl acetate polymer pellets ("Elvax 150," manufactured by DuPont Company, Wilmington, Delaware; an ethylene vinyl acetate random copolymer having 67 wt.% ethylene and 33 wt.% vinyl acetate). A typical concentration is 50 mg. per ml. The pellets can be soaked in methanol for one to two days to extract and/or remove any residual organics and wax therefrom, and thereafter thoroughly dried prior to use. In a like manner using organic solvents, an ultraviolet-light stabilizer solution, an antioxidant solution and a curing agent solution are prepared. The ultraviolet-light stabilizer solution is prepared from Bis(2,2,6,6-tetramethyl-4-piperidiny)l sebacate ("Tinuvin 770," manufactured by Ciba-Geigy Corporation, Hawthorne, New York); the antioxidant solution is prepared from Tris(monononylphenyl)phosphite ("Naugard p," manufactured by Uniroyal Chemical Corporation, Middlebury, Connecticut); and the curing agent solution is prepared from 2,5-Bis(tert-butylldioxy)-2,5dimethylhexane ("Lupersol 101," manufactured by Organic Peroxides Division, Atochem North America Inc., Philadelphia, Pennsylvania). A typical solution concentration consists of 100 pph (parts per hundred) ethylene vinyl acetate, 0.1 wt% stabilizer, 0.2 wt% antioxidant and 1.5 wt% curing agent. Thus, if 50 mg/ml ethylene vinyl acetate is

used, then the stabilizer amount equals 0.05 mg/ml, the antioxidant amount equals 0.10 mg/ml, and the curing agent amount equals 0.75 mg/ml.

The function of the ultraviolet-light stabilizer component is to stabilize the polymer from reacting to ultraviolet light exposure by scavenging for free radicals within the polymer. An antioxidant can be included to function as a polymer stabilizer by stabilizing the polymer during thermal processing and by facilitating the decomposition of (hydro)peroxides. The curing agent initiates the cross-linking reaction between the polymer chains to thereby yield the final product. If included, a primer component, preferably a silane coupling agent such as methacryloxypropyltrimethoxysilane, functions to enhance the adhesion strength of chemical bonding.

A solution mixture containing 100 pph polymer component, 0.1 wt.% ultraviolet-light stabilizer component, 0.2 wt.% antioxidant component and 1.5 wt.% curing agent component was prepared in a vial which was capped tightly and shaken gently on a mechanical shaker for a few minutes. The mixture was then poured into clean Petri dishes with covers and the solvents are allowed to evaporate slowly over one to two days as required. If necessary, a low vacuum at 25-40°C in a vacuum oven can be applied to remove residual solvent. Upon solvent evaporation, a so-called "solution-cast" film is produced in each Petri dish. Because these films are usually fragmented and thin, film pieces are processed together at a temperature of 70-75°C under vacuum for a few minutes in a double-bag vacuum laminator with a spacer between two sheets of Teflon cloth and two metal plates to thereby obtain constant-thickness films. Conversely, a microextruder as known in the art can be used to directly prepare constant-thickness films, thereby eliminating the step requiring preparation of solution cast films.

The constant-thickness films thus produced were then cut to desired sizes and placed between two cleaned quartz or borosilicate glass slide plates of 1/16" to 1/8" thick, placed in the double-bag laminator and laminated and cured. For the curing agent here employed (Lupersol 101), the curing temperature was 145°C for a period of 40 minutes to thereby produce an encapsulating material.

5

Example II

5 In the same manner as in Example I, except for employing as the curing agent component OO-t-butyl-O-(2-ethylhexyl)-monoperoxycarbonate ("Lupersol TBEC," manufactured by Organic Peroxides Division, Atochem North America Inc., Philadelphia, Pennsylvania) and a curing time of eight minutes, a second group of films was prepared.

Example III

10 In the same manner as in Example I, except for employing as the curing agent component 1,1-di(t-butylperoxy)-3,3,5-trimethylcyclohexane ("Lupersol 231," manufactured by Organic Peroxides Division, Atochem North America Inc., Philadelphia, Pennsylvania) and a curing time of eight minutes, a third group of films was prepared.

Example IV

15 In the same manner as in Example I, except for preparing a solution mixture of 100 pph polymer component, 0.1 wt. % ultraviolet-light stabilizer component, 0.2 wt. % antioxidant component, 1.5 wt. % curing agent component and 0.3 wt. % ultraviolet-light absorber component ("Cyasorb UV 531," manufactured by American Cyanamid Corporation, Wayne, New Jersey), a fourth group of films was prepared. The films of Example IV represent the prior-art formulation containing an ultraviolet-light absorber component.

Example V

25 In the same manner as in Example I, except for preparing a solution mixture of 100 pph polymer component and 1.5 wt. % OO-t-butyl-O-(2-ethylhexyl)-monoperoxycarbonate only and without any other additives and for a curing time of eight minutes, a fifth group of films was prepared.

Example VI

30 In the same manner as in Example I, except for preparing a solution mixture of 100 pph polymer component and 1.5 wt. % 2,5Bis(tert-butylldioxy)-2,5-dimethylhexane

only and without any other additives and for a curing time of 40 minutes, a sixth group of films was prepared.

Example VII

In the same manner as in Example I, except for preparing a solution mixture of 100 pph polymer component, 1.5 wt.% OO-tbutyl-O-(2-ethylhexyl)-mono-peroxy carbonate and 0.3 wt.% ultraviolet-light absorber component ("Cyasorb UV 531") only and without any other additives for a curing time of eight minutes, a seventh group of films was prepared.

Sample films from Examples I-VII were exposed to an enhanced ultraviolet light solar simulator for over 2,000 hours at a black panel temperature of 52-54°C. The results of this exposure for Examples I-IV are shown in the graph of Figure 1 and for Examples V-VII in the graph of Figure 2. Specifically, the sample films of Examples IV and VII containing an ultraviolet-light absorber component shows significant yellowing as is apparent in Figures 1 and 2. Conversely, the results vividly demonstrate non-discoloring of encapsulating material not containing an ultraviolet-light absorber component as exemplified in Examples I-III and V-VI. Therefore, the encapsulating material of the present invention maintains clear and colorless characteristics over a practical period of time as photovoltaic devices housed therein operate at efficiency levels significantly above those experienced in devices situated within encapsulating material whose formulation includes an ultraviolet light absorber component. Additionally, an inherent benefit from not using an ultraviolet-light absorber is that the portion of ultraviolet light otherwise absorbed by the absorber becomes available to produce a slight increase in photocurrent.

While an illustrative and presently preferred embodiment of the invention has been described in detail herein, it is to be understood that the inventive concepts may be otherwise variously embodied and employed and that the appended claims are intended to be construed to include such variations except insofar as limited by the prior art.

Claims

1. A substantially clear, substantially colorless encapsulating material for
5 protectively encapsulating an operating photovoltaic device and being substantially free
of an ultraviolet-light absorber component, the encapsulating material comprising a
polymer component and a curing agent component.

2. The encapsulating material of claim 1 wherein the polymer component is
ethylene vinyl acetate.

10 3. The encapsulating material of claim 2 wherein the curing agent component is
selected from the group consisting of 2,5-Bis (tert-butyldioxy)-2,5-dimethylhexane,
00-t-butyl-0-(2-ethylhexyl)-mono-peroxycarbonate and 1,1-di(t-butylperoxy)3,3,5-
trimethylcyclohexane.

4. A substantially clear, substantially colorless encapsulating material for
15 protectively encapsulating an operating photovoltaic device and being substantially free
of an ultraviolet-light absorber component, the encapsulating material comprising a
polymer component, a curing agent component, an antioxidant component and an
ultraviolet-light stabilizer component.

20 5. The encapsulating material of claim 4 wherein the polymer component is
ethylene vinyl acetate.

6. The encapsulating material of claim 5 wherein the curing agent component is
selected from the group consisting of 2,5-Bis (tert-butyldioxy)-2,5-dimethylhexane,
00-t-butyl-0-(2ethylhexyl)-mono-peroxycarbonate and 1,1-di(t-butylperoxy)3,3,5-
trimethylcyclohexane.

25 7. The encapsulating material of claim 5 wherein the antioxidant component is
Tris(mono-nonylphenyl)phosphite.

8. The encapsulating material of claim 6 wherein the antioxidant component is
Tris(mono-nonylphenyl)phosphite.

9. The encapsulating material of claim 5 wherein the ultraviolet-light stabilizer
30 component is Bis(2,2,6,6-tetramethyl4-piperidiny)l sebacate.

10. The encapsulating material of claim 6 wherein the ultraviolet-light stabilizer
component is Bis(2,2,6,6-tetramethyl4-piperidiny)l sebacate.

11. The encapsulating material of claim 7 wherein the ultraviolet-light stabilizer component is Bis(2,2,6,6-tetramethyl4-piperidiny1) sebacate.

12. The encapsulating material of claim 8 wherein the ultraviolet-light stabilizer component is Bis(2,2,6,6-tetramethyl4-piperidiny1) sebacate

Figure 1

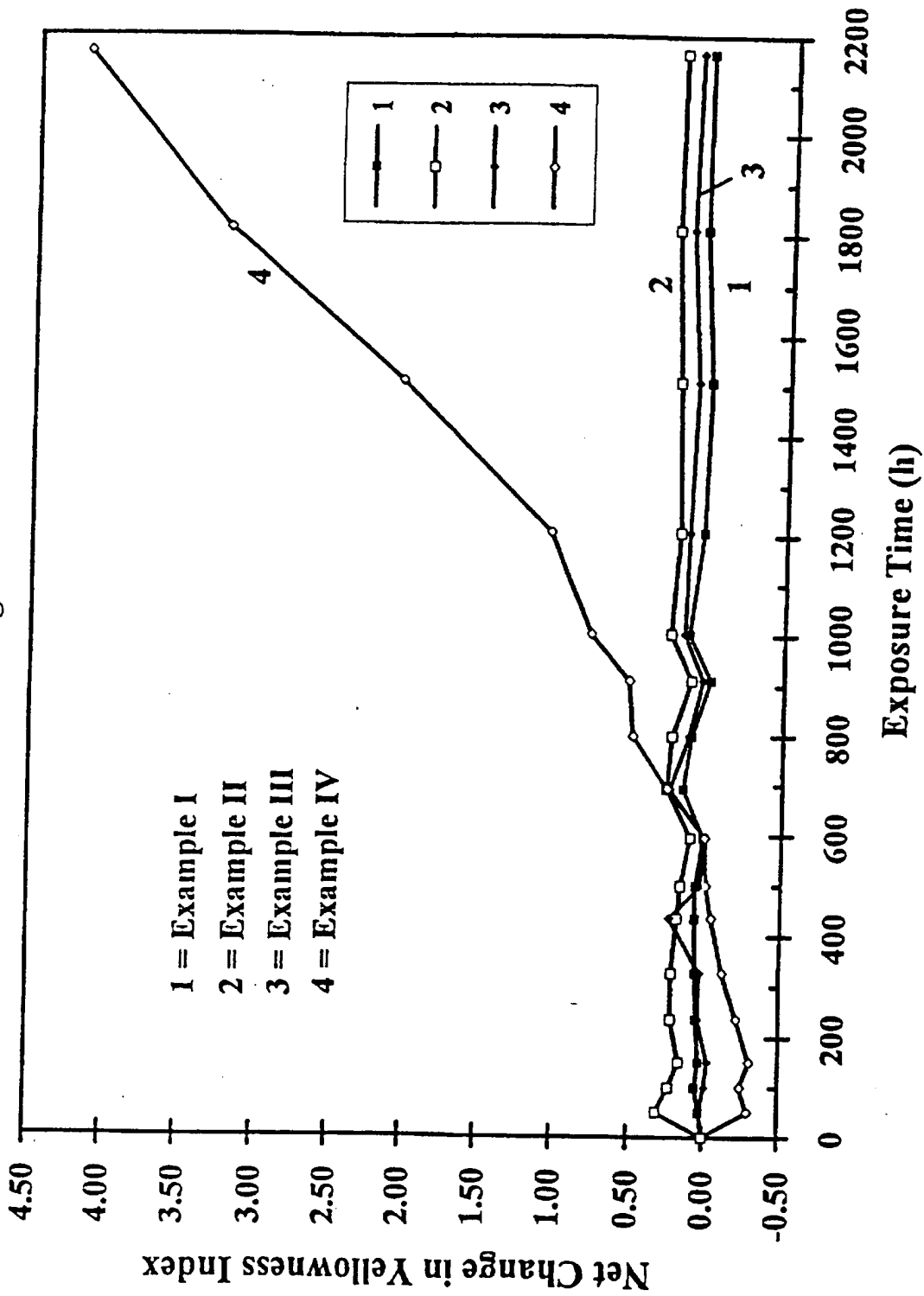
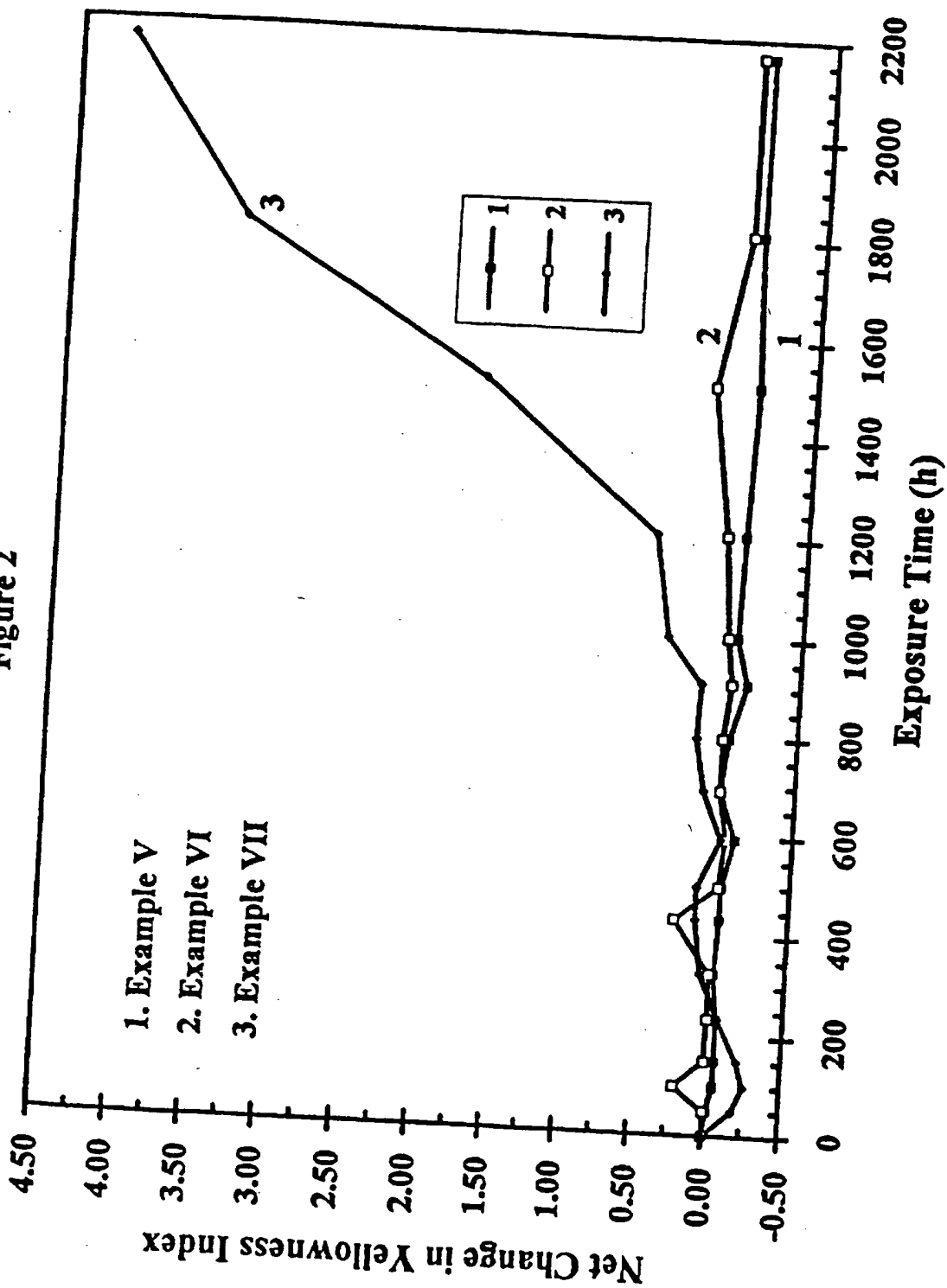


Figure 2



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/20452

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : CO8F 18/08

US CL : 525/330.4

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 525/330.4, 330.3, 333.8, 340, 387

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X --- Y	US 4,499,658 A (K.J. LEWIS) 19 February 1985, columns 1-6, especially column 4, lines 25-38; column 3, line 43; column 6; claim 9.	1-6 ----- 1-12
X --- Y	US 5,447,576 A (P.B. WILLIS) 05 September 1995, columns 1-6, especially column 3, lines 33-38; column 4, lines 41-43; column 6; column 9, lines 58-59; Table 5, column 11.	1-6, 9, 10 ----- 1-12
Y	US 4,348,502 (A.Y. CORAN) 07 September 1982, column 1, lines 23-40, column 4, lines 54-64, column 6, lines 25-26.	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

04 APRIL 1997

Date of mailing of the international search report

15 APR 1997

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/20452

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS

- L1 S ETHYLENE(2W)VINYL ACETATE OR EVA OR "ETHYLENE/VINYL ACETATE"
- L2 S CURING AGENT OR CURATIVE OR CROSSLINK###
- L3 S ANTIOXIDANT
- L4 S (UV OR ULTRAVIOLET)
- L5 S L1(P)L2
- L6 S L5 AND L3
E TRISNONYLPHENYLPHOSPHITE/BI
- L7 S E3
E TRIS(MONONONYLPHENYL)PHOSPHITE/BI
E TRIS(NONYLPHENYL)PHOSPHITE/BI
- L8 S L7 AND L1
- L9 S L8 AND L2
E BIS(2,2,6,6-TETRAMETHYL4PIPERIDINYL)SEBACATE
E SEBACATE
- L10 S SEBACATE
- L11 S L4(P)L10
- L12 S L11(P)L1